CLEAN-BURNING MTBE-FREE GASOLINE FUEL

Background of the Invention

Field of the Invention

The present invention relates to gasoline fuels. In particular, the present invention concerns gasoline fuels free from or having only a low content of water-soluble ethers. The present invention also relates to a method of reducing the emissions of one or more pollutants, selected from the group consisting of CO, NO_x, particulates and hydrocarbons, from an automotive engine.

Description of Related Art

Currently large amounts of water-soluble ethers (e.g. MTBE, methyl tert-butyl ether) are used by petroleum refiners as gasoline components for formulating gasoline products, which, upon combustion in automotive engines, will give rise to low exhaust emissions of harmful pollutants, such as carbon monoxide and nitrogen oxides. To mention an example, present-day Californian grade gasoline, abbreviated CARB II (California Phase II gasoline), contains about 12 vol.-% MTBE and it essentially meets the specifications set by the California Air Resources Board. It has an oxygen content of about 2 %. However, MTBE is water-soluble and biologically very stable, and it may have a tendency to accumulate in groundwater. Thus, the use of water-soluble ethers, such as MTBE, as a component of gasoline fuels will have to be avoided in the future in California and alternative solutions should be found to provide clean-burning high-performance fuels for automotive engines.

Summary of the Invention

It is an aim of the present invention to eliminate the disadvantages of the prior art and to provide a novel gasoline fuel, which is essentially free from water-soluble ethers while still meeting stringent exhaust emission limits.

It is another object of the invention to provide a method of reducing the emissions of an automotive engine of one or more pollutants selected from the group consisting of CO, NOx, particulates and hydrocarbons compared to combusting a CARB II fuel.

These and other objects of the invention and benefits associated therewith will become evident from the following detailed description of the invention.

The present invention is based on the finding that when gasoline fuels without a significant amount of water soluble ethers are produced by blending several hydrocarbon-containing streams together so as to formulate a gasoline product suitable for combustion in a gasoline spark-ignition internal combustion engine, reductions in the emissions of one or more pollutants selected from the group consisting of CO, NOx, particulates and hydrocarbons upon combustion of the gasoline product in such an engine system can be attained by controlling certain chemical and/or physical properties of said gasoline product.

It is well known that olefins, primarily light olefins and in particular tertiary olefins, contribute to the formation of ozone in the atmosphere. However, the relative ozone formation potential of heavy olefins, with a boiling point greater than about 90 °C (194 °F), is very low.

We have found that heavier olefins have a positive effect on the tail pipe emissions and, therefore, it is advantageous to control and minimize the amount of light olefins only in automotive gasoline.

According to the present invention, the content of light olefins, having a boiling point below +90 °C (194 °F), in particular below 85 °C (185 °F), should be less than about 10 vol.-%, preferably less than 6 vol.-% of the gasoline composition. These olefins are made up by C_2-C_6 hydrocarbons. By contrast, the content of heavy olefins having a boiling point above +90°C, preferably above +95°C (203 °F), can be more than 1 vol.-%, preferably 2 vol.-% or more, up to about 30 vol.-%. Suitable heavy olefins contain 8 carbon atoms or more and they are preferably branched. Particularly preferred examples include branched isoolefins containing 8

to 12 carbon atoms, such as trimethylpentenes (isooctenes), trimethylhexenes and trimethylheptenes .

In the fuel, the heavy olefins can used together with paraffines, in particular isoparaffines, such as isooctane, and with alcohols, such as ethanol or methanol.

Thus generally, the invention provides a gasoline fuel composition, having in combination

- an octane value (R+M)/2 of at least 85;
- an aromatics content less than 25 vol. %; and
- a water-soluble ethers content of less than 1 vol. %.

The composition has a content of olefins, at least 10 % of which is formed by heavy olefins having a boiling point above +90 °C. In particular, the composition contains up to 40 % olefins, and it contains less than 6 vol.-% of light olefins having a boiling point below +90 °C, and at least 1 vol.-% heavy branched olefins having a boiling point above +90 °C"

According to an exemplifying embodiment, the present invention concerns an unleaded, clean-burning gasoline fuel with a low content of water-soluble ethers, suitable for combustion in a spark- ignition internal combustion engine and especially in a gasoline direct injection, lean-burning automotive engine having the following properties:

- an octane value (R+M)/2 of at least 85;
- an aromatics content less than 25 vol-%;
- a water-soluble ethers content less than 1 vol-%;
- a 10% D-86 distillation point no greater than +150°F (65.6 °C);
- a 50% D-86 distillation point no greater than +230°F (110 °C);
- a 90% D-86 distillation point no greater than +375°F (190.6 °C);
- Reid Vapor Pressure of less than 9.0 psi (62 kPa);
- a light olefins content, with boiling point below +90°C, less than 6 vol-%; and
- a combined content of trimethylpentenes, trimethylhexenes and trimethylheptenes greater than 1 vol. %.

Reductions in emissions of one or more pollutants selected from the group consisting of CO, NOx, particulates and hydrocarbons compared to combusting a CARB II fuel can be obtained by

a) introducing into said automotive engine an unleaded gasoline having a composition according to any of the above defined gasolines:

b) combusting the unleaded gasoline in said engine;

c) introducing at least some of the resultant engine exhaust emissions into the catalytic converter; and

d) discharging emissions from the catalytic converter to the atmosphere.

Considerable advantages are obtained by the present invention. As will appear from the results presented below, MTBE and similar water-soluble alkyl ethers can be replaced by an increased content of heavier olefins, in particular isoolefins, such as isooctene, in CARB gasoline, without any backsliding of exhaust gas quality. On the contrary, compared to an MTBE-containing fuel, when combusted in a spark ignition internal combustion engine, and particularly in a gasoline direct-injection, lean-burning automotive engine, the present fuels will produce a relatively low amount of gaseous pollutants, in particular one or more of NO_x CO, particulates and unburned or incompletely burned hydrocarbons. Further, there would appear to be a reduction of fuel consumption.

Based on a study commissioned by the EU, there will be no ban on water-soluble alkyl ethers in gasoline in Europe in the foreseeable future, at least within the next 10 or 20 years. It should be pointed out that the present gasoline composition can also be easily converted for use with alkyl ethers by including a desired amount of an alkyl ether as an oxygenate component instead of an alcohol or in addition to that alcohol. In such gasolines, the total concentration of ether + alcohol can be up to 8 vol. % giving rise to an oxygen concentration of 1 to 3 vol.%

Next, the invention will be examined more closely with the aid of the following detailed description with reference to the attached drawings.

Brief Description of the Drawings

Figure 1 shows in the form of a bar chart the total hydrocarbon emissions of six different test cars for six different gasoline compositions;
Figure 2 shows the corresponding bar chart of carbon monoxide emissions;
Figure 3 shows the corresponding bar chart of nitrogen oxide (NOx) emissions;
Figure 4 shows the corresponding bar chart of carbon dioxide emissions;
Figure 5 shows the corresponding bar chart of combined HC and NOx emissions;
Figure 6 shows the corresponding bar chart of particulate matter emissions; and
Figure 7 shows the corresponding bar chart of gasoline consumption.
Figure 8 shows in the form of bar chart the change (%) of the content of methane in exhaust gases compared to fuel RFG for two (E and F) cars of the set of test cars.

Figure 9 shows the corresponding bar chart of 1,3-butadiene content of exhaust gases.

Figure 10 shows the corresponding bar chart of benzene content of exhaust gases.

Figure 11 shows the corresponding bar chart of BTEX compaunds content of exhaust gases.

Figure 12 shows the corresponding bar chart of formaldehyde content of exhaust gases.

Figure 13 shows the corresponding bar chart of acetaldehyde content of exhaust gases.

Figure 14 shows content of polyaromatichydrocarbons (PAH14; EPA PAH) of the particulate matter of the exhaust gases from the two test cars (E and F).

Figure 15 shows the amount of the semivolatile part of particulate matter above.

Figure 16 shows the effect of particulate matter above on the AMES-mutagenicity (rev/mg).

Figure 17 shows the effect of particulate matter above on the AMES-mutagenicity (krev/km).

Detailed Description of the Invention

The present invention relates to a low-emission, gasoline fuel composition, which is essentially free from water-soluble ethers typically used for increasing the octane number of the fuel and for improving the combustion properties thereof. The properties referred to above and in the following are determined by standard test methods outlined in Table 3. Thus, for example, distillation cuts are determined by ISO 3405 (corresponds to ASTM D86), and vapour pressure by EN 13016

The ether content of the present fuel compositions is 1 vol.-% or less, preferably less than 0.6 vol.-%, in particular less than about 0.4 vol.-%. Thus, the gasoline composition is "essentially free from water-soluble ethers".

Typically, the fuel has an octane value (R+M)/2 of at least 85, preferably at least 92, in particular at least 95.

The aromatics content is less than 25 vol. %. It has a total olefins content of more than about 7 vol.-%, typically less than about 40 vol.-%. A considerable part of the olefins are heavy olefins, such as C_{7+} olefins. When the total amount is about 7 vol.%, at least about 15 % of the olefins are heavy, and when the total content is 20 to 30 vol.-%, the heavy olefins make up about 70 vol.-% or more.

It is preferred to limit the total concentration of olefins to about 20 vol.-%.

The preferred heavy olefins are isoolefins comprising 8 to 14 carbon atoms. In particular, the heavy olefins are selected from the group of branched octenes, nonenes and decenes. The following examples can be mentioned: trimethyl-pentenes, trimethylhexenes and trimethylheptenes. The combined content these compounds is 2 to 30 vol. %, and the isooctane, which represents a particularly preferred embodiment, typically stands for a content of 5 to 20 vol. %.

In addition to isoolefins, the present gasoline fuel composition can contain various amounts of paraffines, in particular isoparaffines. The latter are incorporated in amounts of 0.1 to 20 vol.-%, preferably about 1 to 15 vol.-%. According to a preferred embodiment, the total content of isoolefins and isoparaffins is about 2 to 40 vol.-%. Isooctane is a typical isoparaffine, which can be used in up to 20 vol.-%.

The present fuel can also contain various oxygenates, such as alkanols (alcohols). As specific examples, ethanol and methanol can be mentioned. Ethanol-containing compositions contain ethanol in an amount of 0.01 to less than 6 vol.-%. The same concentration range is applicable to methanol. The alkanols can be derived from renewable sources.

By limiting the total concentration of olefins and the maximum concentration of light olefins, and further by using oxygenates it is possible to maintain good combustion properties of the gasoline while reducing emissions.

The concentration of oxygen in the fuel is generally about 0.1 to 5 mass %. Typically, the amount of alkanols is sufficient to provide the gasoline composition with an oxygen content of about 1 to 4 mass-%.

A fuel according to the present invention exhibits the following characteristics:

- a 10 % D-86 distillation point no greater than +150 °F (65.6 °C), in particular less than 140 °F (60 °C);
- a 50 % D-86 distillation point no greater than +230 °F (110 °C), in particular less than 220 °F (104.4 °C);
- a 90 % D-86 distillation point no greater than +375 °F (190.6 °C), in particular less than 370 °F (187.8 °C); and

  a Reid Vapor Pressure less than 9.0 psi (62 kPa), in particular less than 8.5 psi (58.6 kPa).

Based on experimental data, the particulate matter emissions were 50 % lower than those of a conventional CARB II fuel, and the emissions of THC, NOx, CO and CO_2 were on the same level or lower as for CARB II fuels.

The experimental results shown below indicate that it is fully possible to provide gasoline compositions which are free from water-soluble and which, nevertheless, meet even stringent requirements for low emissions, by increasing the concentration of heavy olefins and by simultaneously reducing the concentration of light olefins.

The following, non-limiting example will elucidate the invention:

Example

The composition of the gasoline is basically determined by the CARB specification. The present invention provides for a modification of that specification by the combined use of heavy olefins and isoparaffines, in particular isooctene and isooctane, optionally with oxygenates, in particular ethanol.

The exhaust emission tests were carried out with six different fuels. The fuels and their compositions are shown in Table 1 below:

Table 1. Compositions of Test Fuels

TEST FUELS	*Isooctane*	*Isooctene*	*NExTAME*	*Ethanol*	*MTBE*	*Oxygen w-%*	*Olefins vol-%*	*Aromatics vol-%*	
RFG			X		X	2	15	35	*ref*
CARB II					X	2	5	25	*ref*
CARB III IO	X			X		2	5	25	
CARB III IOE	X	X		X		2	15	25	
IsoOkt	X						5	25	
IsoOkte	X	X					15	25	

In the above table, the following abbreviations are used:

RFG Reformulated gasoline, Porvoo refinery sales grade into Finnish markets, Fulfils EU 2005 requirements, our reference in all of our measurements

CARB II Californian grade gasoline containing **MTBE**, California Phase II gasoline (MTBE gasoline) that almost meets the specifications set by the California Air Resources Board

CARB III IO Californian grade gasoline containing **ethanol and isooctane**, Future California Phase III gasoline without MTBE, but containing oxygen

CARB III IOE Californian grade gasoline containing ethanol, isooctane and isooctene, Future California Phase III gasoline without MTBE, but containing oxygen, like **CARB III IO**, but 10 vol-% of paraffins and isoparaffins have been replaced by **heavy olefins** (isooctene)

IsoOkt Like Californian grade gasoline **without any oxygenates**, isooctane gasoline where the MTBE has been replaced with isooctane

IsoOkte Like Californian grade gasoline **without any oxygenates**, isooctane gasoline where the MTBE has been replaced with isooctane, like **IsoOkt**, but 10 vol-% of paraffins and isoparaffins have been replaced by **heavy olefins** (isooctane)

In RFG, the concentration of TAME was 18 vol.-% and of MTBE 5 vol.-%. In CARB II, the concentration of MTBE was 12 vol.-%.

In the rest of the fuel compositions, the concentration of isooctane was 11 vol.-% and in CARB III IO and IsoOkte, the concentration of isooctane was 10 vol.%.

The properties of the isooctane and isooctene components, obtained from the Fortum NExOCTANE pilot plant in Porvoo, Finland, are given in Table **2**.

Table 2. Properties of isooctane and isooctane components.

Property	Method	Isooctane	Isooctane
RON	ISO 5164	100.5	101,6
MON	ISO 5163	98.3	84,6
Vapor pressure [kPa]		15,9	14
Density [kg/m3]		701	729
T10 distillation point [°C]	ASTM D86	98	102
T50 distillation point [°C]	ASTM D86	100	105
T90 distillation point [°C]	ASTM D86	119	117
Olefin content, GC [% by volume]		0,5	97
Aromatics content, GC [% by volume]		0	0
Saturates, GC [% by volume]		99,5	0

Properties of the test fuels are presented in Table 3.

Table 3. Properties of test fuels

		Code	RFG	CARB II	CARB III IO	CARB III IOE	IsoOkt	IsoOkte
Density at +15°C	ISO 12185	kg/m³	766	742	745	745	736	737
Sulphur	ASTM D 3120	ppm	25	10	11	12	10	9
Vapour Pressure	EN 13016	kPa	62	59	61	63	60	61
FIA-O	**ISO 3837**							
Arom		Vol-%	37	27	25	25	25	26
Olef		Vol-%	13	5	4	14	3	14
Paraf+Naph		Vol-%	38	58	65	55	72	60
Oxygenates		Vol-%	12	11	5	6	0	0
Total			100	100	100	100	100	100
C/H-ratio			6.93	6.49	6.45	6.56	6.50	6.59
Content of Hydrogen	NMR	mass-%	12.70	13,50	13.60	13.50	14.00	13.70
Benzene	GC	mass-%	0.70	0,37	0.35	0.39	0.34	0.37
EtOH	AED	Vol-%			5,46	5.36	0.00	0.00
TAME	AED	Vol-%	5.55	0,02	0.02	0.00	0.00	0.00
MTBE	AED	Vol-%	4.48	11,09	0.02	0.03	0.03	0.04
Other Oxygenates		Vol-%		0,04		0.00	0.00	0.00
Distillation	**ISO 3405**							
IBP		°C	33.4	29,3	35.4	32.9	28.5	33.0
05 til-%		°C	45.0	42.9	45.0	47.4	43.4	45.6
10 til-%		°C	54.0	50.5	51.8	52.4	53.6	54.2
20 til-%		°C	69.3	59.5	59.1	59.3	68.5	67.7
30 til-%		°C	81.6	68,0	66.6	67.2	81.6	79.8
40 til-%		°C	92.7	77.5	87.4	85.7	92.7	91.4
50 til-%		°C	103.0	88.7	101.0	98.9	101.3	100.4
60 til-%		°C	114.5	101.8	108.3	106.6	108.1	107.3
70 til-%		°C	126.7	114.8	116.4	114.4	115.2	114.5
80 til-%		°C	140.4	127.8	127.7	125.5	126.3	125.5
90 til-%		°C	155.3	147.5	148.5	146.3	147.7	146.8
95 til-%		°C	165.3	159.6	159.9	158.3	160.5	161.0
FBP		°C	196.6	189.7	190.1	187.6	189.6	190.7

Emissions were measured at 22 °C temperature for 6 vehicles using the European cycle for year 2000 (ECE+EUDC). Five of the vehicles have 4-cylinder, 16-valve engines equipped with multi point fuel injection (MPI) and a three-way catalytic converter (TWC). The swept volume of these vehicles A, B, C, D and F was form 1.3 liter to 2.0 liter . On e vehicle (E) has the engine with six cylinder and the swept volume of 3.3 liters. Also this vehicle was equipped with multi point fuel injection (MPI) and a three-way catalytic converter (TWC

EMISSION TESTING – Exhaust emissions and fuel consumption of the vehicles were measured on a chassis dynamometer using the current European test cycle according to 70/220/EEC and its amendments. The test equipment used for exhaust dilution, collection of samples and analysis of samples are in compliance with the specifications of US EPA and directive 70/220/EEC and its amendments.

SAMPLING AND ANALYSES OF PARTICULATE AND SEMIVOLATILE MATTER – Particulates were collected at Fortum using a high capacity system and at the Technical Research Centre of Finland (VTT) using a similar system. The test procedure, sampling and analyses of particulate and semi-volatile matter was performed in a similar way as described by Kokko et al. [Kokko, J., Rantanen, L., Pentikäinen, J., Honkanen, T., Aakko, P., and Lappi, M., Reduced Particulate Emissions with Reformulated Gasoline, SAE Technical Paper 2000-01-2017, 2000]. Sampling and analytical procedures for the particulate and semi-volatile phases at both Fortum and VTT laboratories are briefly described in Lappi, M., Harmonisation of measuring methods of unregulated exhausts from passenger cars. Results of the Round-robin tests. Final report. VTT Energy Engine Technology. Mobile Research Program. Project 232T. March 1999. 50 p. + App. 119 p.

<u>THC Emissions</u> – The total hydrocarbon emissions are presented in Figure 1. The THC emissions from the vehicles using a catalytic converter are with near all of the vehicles tested lower with the gasolines according to the present invention than with the other gasolines.

<u>CO Emissions</u> – Values presented in Figure 2 show that, compared to CARB II, the carbon monoxide emissions are lower for five vehicles for CARB III IOE, whereas they are somewhat higher for ISO-OKTE. This confirms that the effect of oxygen in gasoline can be significant when reducing CO emissions especially in vehicles without closed loop fuel control systems.

<u>NO_X Emissions</u> – Generally, gasoline with oxygenates slightly increases NO_X emissions, and this was also found to be the case in this study, but lower for the gasolines according to the present invention compared to CARB II with all cars tested.

<u>CO_2 Emissions and fuel consumption</u> – The carbon dioxide emissions and gasoline consumption of the test vehicles are presented in Figures 4 and 7. CO_2 emissions from all the gasolines are almost equal and the possible differences are within the confidence interval. All the differences fall within the confidence interval. Fuel consumption for the fuels with no oxygenates were lower than with oxygenates as expected.

Non-controlled emissions- With the two test cars (E and F) also the amount of so called non-controlled exhaust emissions were measured (Figures 8 to 13). From the figures can be seen that the results are more depending on the car measured than on the fuel tested. And no big differences cannot be seen.

PARTICULATE MASS EMISSIONS – The average particulate mass emissions at 22 °C with the two fuels and all vehicles are given in Figure 6. Results are presented as average values derived from three or four tests on each fuel. Confidence intervals for these mean values are shown at the 95% level. With catalyst equipped vehicles the amount of particulate mass collected on the filters is very small compared to the weight of blank filters and thus the standard deviation of the results is rather high. Therefore the confidence intervals are quite large. Nevertheless, the gasolines according to the present invention have extremely low particulate mass emissions compared to all other gasolines, including CARB II.

The toxic and mutagenic promerties of the particulate matter of the exhaust gases from the two test cars are represented in Figures 14 to 17. It can be seen that toxicity and the mutagenicity of the particulates with the fuel of the present invention were lower when compared to CARB II with all cars tested.

As the above test results, it is fully possible to replace MTBE in gasoline with heavy olefins without impairing the air quality of exhause gases.